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SERIAL NUMBER :

TITLE : RARE EARTH METAL COMPOUNDS FOR USE IN
HIGH CRITICAL TEMPERATURE THIN FILM SUPER-
CONDUCTORS, FERROELECTRICS, PYROELECTRICS,
PIEZOELECTRICS, AND HYBRIDS

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CONTINUATION-IN-PART

This application is a continuation in part of U.S. Patent and Trademark Office Application Number 09/337,724, entitled, "Rare Earth Metal Containing Compounds and High Critical Temperature Thin Film Superconductors, Ferroelectrics, Pyroelectrics, Piezoelectrics and Hybrids Including the Rare Earth Metal Containing Compounds," filed on June 21, 1999, and designated as CECOM Docket No. 5433, which was a continuation in part of U.S. Patent and Trademark Office Application Number 08/717,822 with the same title, filed on September 24, 1996 and designated as CECOM Docket No. 5304. That application (Serial No. 08/717,822) was a continuation in part of U.S. Patent and Trademark Office Application Number 08/333,669 with the same title, filed on November 3, 1994 and designated as CECOM Docket No. 5097. This continuation in part is being filed under 37 CFR. § 1.53.

RELATED APPLICATION

CECOM Docket No. 5151, assigned U.S. Patent Office Application No. 08/502,739, enti-

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tled "Compounds in the Series A_2MeSbO_6 for Use as Substrates, Barrier-Dielectric Layers and Passivating Layers in High Critical Temperature Superconducting Devices," which has been assigned to the same assignee issued as U.S. Patent Serial No. 5,814,584 on April 29, 1998 and is related to this application.

GOVERNMENT INTEREST

The invention described herein may be manufactured, used, and licensed by or for the Government for governmental purposes without the payment to us of any royalties thereon.

FIELD OF INVENTION

The invention relates in general to new and useful rare earth metal containing compounds, and in particular to new uses for compounds of the general formula Sr_2RESbO_6 where RE is a rare earth metal.

BACKGROUND OF THE INVENTION

Heretofore, the best substrate or barrier dielectric in thin film superconductor technology has been $LaAlO_3$. However, there have been problems with the use of $LaAlO_3$. For one, its dielectric constant is anisotropic and too high. This automatically prevents one from making certain types of devices. It also undergoes a phase transition leading to twinning and stress. The present invention provides a solution to many of the shortcomings and problems associated with the use of $LaAlO_3$.

SUMMARY OF THE INVENTION

The general object of this invention is to provide materials that can be used as a substrate or barrier dielectric in thin film superconductor technology that can overcome the problems, shortcomings and limitations of $LaAlO_3$. A more particular object of the invention is to provide a substrate or barrier dielectric with a low dielectric constant, a low dielectric loss, and a material that does not undergo a phase transition that leads to twinning and stress. It is a further object of

the present invention to provide compounds and structures producing tetragonal phases that are extremely useful as dielectric substrates and buffer layers for YBCO and other thin film superconductor devices.

It has now been found that the aforementioned objects can be attained using a compound of the general formula $\text{Sr}_2\text{RESbO}_6$ where RE is a rare earth metal as the substrate or barrier dielectric in thin film superconductor technology. In the above formula, RE can be Lu, Yb, Tm, Er, Ho, Dy, Tb, La, Pr, Y Sm, Nd, Eu or Gd. These compounds can be used as barrier or buffer layers and substrates in thin film high critical temperature superconducting structures, as well as antennas and other devices such as ferroelectrics, pyroelectrics, piezoelectrics and hybrids.

DESCRIPTION OF THE INVENTION

Indexed powder diffractometer data taken using $\text{CuK}\alpha$ radiation, reveals these compounds to be ordered perovskites. With the exceptions of $\text{Sr}_2\text{LuSbO}_6$ and $\text{Sr}_2\text{LaSbO}_6$ that are cubic, all of the other compounds are found to be pseudo-cubic, tetragonal. Single and multilayer thin films are prepared by KrF pulsed laser ablation. By thin films is meant film thicknesses ranging from about 100Å to about 10 μm . All $\text{Sr}_2\text{RESbO}_6$ films exhibit a primary (h00) and a secondary (2n, 2n,0) orientation. Dielectric constants and losses are measured in bulk samples by a cavity perturbation technique at X band and on films by an impedance bridge at 1 MHz. The term "low dielectric loss," as used throughout this disclosure, is defined as any dielectric loss lower than 1×10^{-2} . The term "low dielectric constant," as used throughout this disclosure, is defined as any dielectric constant lower than 20, and, in this invention ranges from 5.1-16.3 in the bulk form and from 4.1-16.3 in the thin film form, within an experimental error of +/- 5 %. Results are given in the TABLE I, below and while dielectric constants for thin films are generally similar to the bulk values, factors such as density differences between the bulk and thin film samples result in differences in dielectric constant in some cases.

The following compounds in the series $\text{Sr}_2\text{RESbO}_6$ have been synthesized for use as dielectric substrates or barrier layers or passivation layers in thin film high critical temperature superconductor devices:

TABLE I

Compound Formula	Lattice Parameter (Å)			Density GM/CC	Dielectric Constant		Dielectric Loss Factor X 10 ⁻³		Color
	a	c	c/a		BULK	FILM	BULK	FILM	
Sr ₂ LaSbO ₆	8.325	--	1.0	5.91	16.3	--	3.8	--	beige
Sr ₂ PrSbO ₆	8.390	8.362	.9966	6.02	10.9	--	2.2	--	d. gray*
Sr ₂ NdSbO ₆	8.365	8.320	.9946	6.13	10.6	--	2.9	--	beige
Sr ₂ SmSbO ₆	8.335	8.295	.9952	6.26	13.6	8.8	<1	9	d. beige
Sr ₂ EuSbO ₆	8.320	8.300	.9975	6.30	14.6	4.6	<1	2	l. yellow*
Sr ₂ GdSbO ₆	8.295	8.280	.9978	6.42	12.1	6.0	<1	9	beige
Sr ₂ TbSbO ₆	8.280	8.248	.9961	6.48	12.9	4.6	1.4	4	beige
Sr ₂ HoSbO ₆	8.239	8.218	.9975	6.64	11.6	--	--	3.1	white
Sr ₂ DySbO ₆	8.248	8.224	.9971	6.64	11.2	--	<1	--	beige
Sr ₂ ErSbO ₆	8.222	8.204	.9974	6.77	5.3	4.1	1.6	3.2	white
Sr ₂ TmSbO ₆	8.204	8.185	.9976	6.86	10.0	--	2.0	--	white
Sr ₂ YbSbO ₆	8.190	8.176	.9985	5.87	5.1	--	<1	--	white
Sr ₂ YSbO ₆	8.231	8.216	.9982	6.56	7.1	--	1.4	--	white
Sr ₂ LuSbO ₆	8.188	--	1.0	6.90	15.1	--	<1	--	beige

* "d" denotes dark and "l" denotes light

Note that all compounds exhibit dielectric constants far superior (lower) than LaAlO₃(22) and some superior to MgO(10). Based on an experimental error of +/- 5 %, the following thin film dielectric loss values are expected: 14.5-16.1 for Sr₂LaSbO₆; 10.4-11.4 for Sr₂PrSbO₆; 10.1-11.1 for Sr₂NdSbO₆; 11.1-12.2 for Sr₂HoSbO₆; 10.6-11.8 for Sr₂DySbO₆; 9.5-10.5 for Sr₂TmSbO₆; 4.8-5.4 for Sr₂YbSbO₆; 6.7-7.5 for Sr₂YSbO₆; and 14.3-15.9 for Sr₂LuSbO₆. The thin film values for dielectric losses in the Sr₂LaSbO₆; Sr₂PrSbO₆; Sr₂NdSbO₆; Sr₂HoSbO₆; Sr₂DySbO₆; Sr₂TmSbO₆; Sr₂YbSbO₆; Sr₂YSbO₆; and Sr₂LuSbO₆ compounds would be expected to be equivalent to the TABLE I empirical bulk values reported above.

All compounds exhibit properties making their use advantageous as dielectric substrates, buffer layers, in antenna structures and a number of superconductor structures. Pulsed laser

ablation targets of the compounds containing rare earths are prepared as follows:

Stoichiometric amounts of SrCO_3 , the rare earth oxides and Sb_2O_3 are weighed out, mixed together in a mortar, pressed into a disc and calcined at 1000°C for 15 hours, then cooled to room temperature. The disc is ground in a mill to a particle size = $100\text{ }\mu\text{m}$, repressed into a disc, calcined at 1100°C for 15 hours and cooled to room temperature. The discs are ground to a powder, pressed into a disc and heated a second time to $1200\text{--}1300^\circ\text{C}$ for 10-15 hours and cooled to room temperature. The disc is reground to a particle size of $100\text{ }\mu\text{m}$, pressed into a $1\frac{1}{4}$ inch disc, isostatically pressed at 60000 PSI, sintered at $1400\text{--}1600^\circ\text{C}$ for 20 hours and slow cooled to room temperature. In this connection, by bulk is meant dense sintered polycrystalline bodies from about 1 to 1.25 inch in diameter and about 0.125 inch to $\frac{1}{4}$ inch thick. X-ray diffractometer traces are run to confirm that each disc is single phase and the lattice parameters are calculated from the indexed pattern. These compounds are distorted from cubic. They are indexed on the basis of a tetragonal unit cell with two exceptions, $\text{Sr}_2\text{LuSbO}_6$ and $\text{Sr}_2\text{LaSbO}_6$ that are cubic. See TABLE I. All these compounds form an ordered perovskite structure in which alternate B site ions are occupied by Sb and a rare earth ion. This gives rise to weak reflections in the X-Ray diffraction powder pattern that requires doubling of the unit cell.

It is important to note the significant relationship between the higher temperatures of 1400°C and 1600°C for 20-50 hours and the densities attained with these materials. The papers "Dielectric constants of yttrium and rare-earth garnets, the polarizability of gallium oxide and the oxide additivity rule," by R.D. Shannon et al. and " Dielectric polarizabilities of ions in oxides and fluorides," by R.D. Shannon established that the dielectric constant of a well-behaved complex oxide can be predicted by knowing the polarizability of the atoms making up the structure and the volume of the structure. From these relationships it is straightforward to understand that the dielectric constant of a material is sensitive to the sample's density. For instance, the more porous the sample (i.e. less dense), the lower the dielectric constant will be (air has a dielectric constant of roughly 1.00 for a sample density approaching 0%). When comparing two samples of the same compound with equivalent densities, e.g. both 100 % dense, the same dielectric constant would be expected. However, when comparing two material samples with different densities and the same lattice parameter, the dielectric constant measurements can be appreciably different, again dependent on the difference in sample density.

Further, the polarizability of Sb^{5+} , which is a constituent atom of the materials used to

fabricate the compounds and devices of the present invention, has not been previously known. The materials of the present invention all include at least one Sb^{5+} constituent atom with a polarizability of about 1.2 \AA^3 . Therefore, prior art references that do not account for significant factors such as polarizability and material density have not predicted the advantageous dielectric constants of the materials of the present invention.

Additionally, it should be noted that only two of the compounds in the series $\text{Sr}_2\text{RESbO}_6$ were cubic: $\text{Sr}_2\text{LuSbO}_6$ and $\text{Sr}_2\text{LaSbO}_6$, both being ordered with a 1:1 distribution of RE and Sb on B sites, with a perovskite ideally being ABO_3 . The ordering leads to a doubling of the unit cell. We have discovered that in order to achieve an ordered cubic single phase material, sintering at 1600°C for at least 20 hours in the case of $\text{Sr}_2\text{LuSbO}_6$ and 1400°C for $\text{Sr}_2\text{LaSbO}_6$ for at least 20 hours were essential. It is also noted that the cubic ordered perovskites prepared in connection with the present invention are quite different from those found in the literature because the compounds disclosed herein were prepared at higher temperatures for a longer period of time. The other compounds disclosed herein are similarly ordered but are pseudo-cubic, or tetragonal perovskites, which, except for $\text{Sr}_2\text{NdSbO}_6$, required sintering at temperatures between 1450°C and 1600°C for a minimum of 10 hours to achieve the tetragonal phase.

LaAlO_3 and MgO are often used as substrates on which high critical temperature superconducting film such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) films are grown for device applications. The lattice mismatch for heteroepitaxial growth of YBCO on LaAlO_3 is outstanding, about 1%. For MgO it is about 7%. The mismatch in lattice parameter for the $\text{Sr}_2\text{RESbO}_6$ compounds epitaxially grown on YBCO is given in TABLE II, below. While their mismatch does not compare favorably with LaAlO_3 , several compounds compare favorably with MgO . In general, the combination of lattice match, low dielectric constant, low dielectric loss, and absence of lattice strain and twinning due to phase transformation make these compounds superior to either LaAlO_3 or MgO .

TABLE II
% MISFIT TO YBCO

COMPOUND	a-LATTICE PARAMETER	% MISFIT TO	
		a YBCO	b YBCO
$\text{Sr}_2\text{LaSbO}_6$	8.325	8.2	6.5
$\text{Sr}_2\text{PrSbO}_6$	8.390	8.9	7.2
$\text{Sr}_2\text{NdSbO}_6$	8.370	8.7	7.0
$\text{Sr}_2\text{SmSbO}_6$	8.330	8.3	6.6
$\text{Sr}_2\text{EuSbO}_6$	8.320	8.2	6.5
$\text{Sr}_2\text{GdSbO}_6$	8.295	7.7	6.2
$\text{Sr}_2\text{TbSbO}_6$	8.280	7.7	6.0
$\text{Sr}_2\text{DySbO}_6$	8.248	7.3	5.7
$\text{Sr}_2\text{HoSbO}_6$	8.329	7.2	5.6
$\text{Sr}_2\text{ErSbO}_6$	8.222	7.1	5.3
$\text{Sr}_2\text{TmSbO}_6$	8.204	6.9	5.2
$\text{Sr}_2\text{YbSbO}_6$	8.190	6.7	5.0
Sr_2YSbO_6	8.231	7.1	5.4
$\text{Sr}_2\text{LuSbO}_6$	8.188	6.6	4.9

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Experimental conditions used to obtain single and multilayered structures by laser ablation are described below: Thin films of $\text{Sr}_2\text{RESbO}_6$ (where RE = Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) are deposited using the pulsed laser deposition technique. The

KrF excimer laser ($\lambda = 248$ nm) parameters are a pulse repetition rate of 10Hz and a laser fluence of 1-2 J/cm² at the target (unless noted otherwise in TABLE III). Chamber deposition conditions are listed in TABLE III.

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TABLE III

Ar#	Material	Substrate		Oxygen Pressure (mTorr)	Block Temp(°C)
		MgO	YBCO/MgO		
564	Sr ₂ YSbO ₆	X		170	800
	Sr ₂ LaSbO ₆				
	Sr ₂ PrSbO ₆				
	Sr ₂ NdSbO ₆				
593a	Sr ₂ SmSbO ₆		X	170	750
615	Sr ₂ EuSbO ₆		X	100	750
593d	Sr ₂ GdSbO ₆		X	170	800
614	Sr ₂ TbSbO ₆		X	250	750
593c			X	170	800
613	Sr ₂ DySbO ₆		X	170	750
790	Sr ₂ HoSbO ₆	X	X	130	825
593c	Sr ₂ ErSbO ₆		X	170	800
684*	Sr ₂ TmSbO ₆	X		250	785
618			X	100	750
792	Sr ₂ YbSbO ₆	X	X	130	825

685*			X	250	785
565			X	170	800
789	Sr ₂ LuSbO ₆	X	X	130	825
* 20 Hz laser repetition rate.					

X-Ray diffraction analysis of the single layer films, Sr₂RESbO₆/MgO reveals that (400) is the strongest reflection with (200) weaker. However, (220) is strong and (440) weak but both are subsidiary to (400) and (200). For Sr₂RESbO₆/YBCO/MgO (400) and (200) are the primary reflections. (220) and (440) are present but now they are much weaker. Specific results are given in TABLE IV, below.

TABLE IV

STRUCTURE	OBSERVED X-RAY REFLECTIONS			SAMPLE NO.
	YBCO	Mg O	ANTIMONATE	
Sr ₂ YbSbO ₆ /MgO	003	002	200 strong	AR# 612
	005		220 strong	
	006		400 very very weak	
	007		404 very weak	
	008			
	009			
Sr ₂ TmSbO ₆ /YBCO/MgO	003	002	200 weak	AR# 618
	005		220 very weak	

	006 007 009	400	400 very weak	
$\text{Sr}_2\text{EuSbO}_6/\text{YBCO}/\text{MgO}$	003 005 006 007 008	200	moderate 400 very very strong	AR# 615
$\text{Sr}_2\text{SmSbO}_6/\text{YBCO}/\text{MgO}$	003 005 006 007 008	200	200 very strong 220 moderate 400 very very strong	AR# 593A
$\text{Sr}_2\text{YSbO}_6/\text{Mgo}$		200 400	200 strong 220 strong 400 very strong 440 weak 600/442 weak	
$\text{Sr}_2\text{LuSbO}_6/\text{YBCO}/\text{MgO}$	003 005 006 007 009 0,0,10 0,0,11	200 400	200 strong 220 weak 400 very very strong 440 very weak 442 moderate 800 very strong	AR# 789
$\text{Sr}_2\text{YSbO}_6/\text{MgO}$		200 220	200 weak 220 strong 400 strong 440 weak	AR# 792

			444 weak	
$\text{Sr}_2\text{HoSbO}_6/\text{MgO}$		200 400	200 moderate 220 strong 400 very strong 440 moderate	AR# 790
$\text{Sr}_2\text{HoSbO}_6/\text{YBCO}/\text{MgO}$	003 005 006 007 008 009 0,0,10	200 400	200 strong 220 moderate 400 very strong 440 weak	AR# 790
$\text{Sr}_2\text{TmSbO}_6/\text{YBCO}/\text{MgO}$	003 005 006 007 008	200 400	200 moderate 220 weak 400 strong 440 weak	AR# 684
$\text{Sr}_2\text{ErSbO}_6/\text{YBCO}/\text{MgO}$	003 005 006 007 008	200 400	200 strong 220 weak 400 very strong	AR# 593C
$\text{Sr}_2\text{EuSbO}_6/\text{YBCO}/\text{MgO}$	003 005 006 007 008 009	200 400	200 moderate 220 weak 400 very strong	AR# 615

	0,0,10			
Sr ₂ TbSbO ₆ /YBCO/MgO	003	200	200 moderate	AR# 614
	005	400	220 weak	
	006		400 strong	
	007		800 weak	
	009			
	0,0,10			
	0,0,11			
Sr ₂ SmSbO ₆ /YBCO/MgO	003	200	200 strong	AR# 593A
	005	400	220 moderate	
	006		400 very strong	
	007			

The quality of Sr₂RESbO₆ thin films on MgO and YBCO/MgO are very high judging from the surface reflectivity and the very large intensity of the (400) reflections. The latter implies an excellent approach to epitaxial growth especially with respect to YBCO.

Microwave measurements of real and imaginary parts of the dielectric constant of bulk Sr₂RESbO₆ are performed at approximately 9.32 and 10.1 GHz and room temperature. A cavity perturbation technique is used with a reflection-type, rectangular cavity excited in either the TE₁₀₆ mode (for 9.3 GHz) or the TE₁₀₇ mode (for 10.1 GHz). The cavity is coupled to the waveguide by an adjustable iris having a 0.5 mm side by 35 mm long slot (cut along the center of one of the broad sides) providing access for the thin, rectangular samples cut from bulk Sr₂RESbO₆ polycrystalline discs. The samples are held such that their long dimension is parallel to the E-field of the cavity and they are positioned at the E-field maximum as determined by maximizing the shift of the cavity.

The real part of the dielectric constant is calculated from the shift in resonance frequency of the cavity due to the sample, and the imaginary component is calculated from a change in cavity Q. The accuracy of these measurements depends upon two general sources of error: 1) The accuracy of the cavity characterization; and 2) the material properties such as density and uniformity of shape. The error due to the cavity characterization results in an accuracy of

approximately $\pm 2\%$ for the real part of the dielectric constant, and limits the resolution of the loss tangent (the imaginary component divided by the real component of the dielectric constant) to approximately 0.001. The error due to material properties and sample shape can be considerably greater than the cavity characterization error, particularly the error due to low material density, hence the densities of bulk materials are reported in the Density GM/CC column of TABLE I.

For thin films, the dielectric constant and loss are obtained by an impedance measurement at 1 MHz. These films are prepared by depositing the appropriate $\text{Sr}_2\text{RESbO}_6$ compound as a film by pulsed laser ablation on a (001) oriented YBCO on (100) oriented MgO substrate, see TABLE III, above. Films with dielectric constants lower than those obtained from bulk measurements may be due to low density in the film, higher octahedral site ordering and/or measurement used (i.e. the large difference may arise from the large difference in frequencies 1MHz versus 10^6Hz).

The compounds of the system $\text{Sr}_2\text{RESbO}_6$ are psuedo-cubic with departure from cubicity of 0.1% or less with $\text{Sr}_2\text{LuSbO}_6$ and $\text{Sr}_2\text{LaSbO}_6$ that are cubic. The dielectric constants are much lower than LaAlO_3 (22-25) and generally range from 5-16, however, even lower dielectric constants of 4.1-4.6 are reported for several thin films listed in TABLE I, and the much lower dielectric constant achieved herein is an important factor contributing toward the usefulness of the compounds disclosed herein in numerous structures and devices such as dielectric substrates, buffer layers, antennas, thin films and so on.

In the foregoing disclosure, by the term "high critical temperature thin film superconductor device" is meant a copper oxide superconductor having a critical temperature in excess of 30 K. Examples of such superconductors are: $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{REBa}_2\text{Cu}_4\text{O}_8$ where RE is a rare earth element and $0 \leq \delta \leq 1$, $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$, $\text{Tl}_1\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_9$, and $\text{Tl}_2\text{Ba}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ as well as Hg-based superconductors.

A single layer device refers to a device including a single layer of high critical temperature superconducting ferroelectric, pyroelectric, piezoelectric, or ferromagnetic material. A multi-layer device refers to a device including at least two layers of a high critical temperature superconductor, ferroelectric, pyroelectric, piezoelectric, dielectric or ferromagnetic materials.

High critical temperature superconducting, dielectric, ferroelectric, pyroelectric, piezoelectric, and ferromagnetic materials and the compounds of this invention can be used in

numerous devices including flux flow transistors, current limiters, broadband impedance transformers, diodes, delay lines, resonators, antenna, antenna feeds, switches, phase shifters, mixers, amplifiers, balometers and magneto-resistors.

The compounds of the invention can be made in the form of a bulk single crystal substrate, a dense polycrystalline disc, a crystalline epitaxial thin film or a polycrystalline thin film. In their manufacture, some form of laser ablation is preferred, but the compounds can also be made by sputtering, MOCVD, MBE, evaporation, etc.

In addition to numerous device uses already disclosed throughout this specification, the following examples illustrate two specific uses of the $\text{Sr}_2\text{RESbO}_6$ compounds of this invention.

An antenna can be made according to the invention by depositing a single layer of high critical temperature superconductor (HTSC) directly onto a single crystal $\text{Sr}_2\text{LuSbO}_6$ substrate or a substrate of other composition buffered with a layer of $\text{Sr}_2\text{LuSbO}_6$. The HTSC is then patterned to complete the device.

A superconductor insulator superconductor step edge Josephson junction, a multilayer superconducting device, is fabricated according to the invention using $\text{Sr}_2\text{YbSbO}_6$. More particularly, the device is made by depositing a single layer of HTSC on a single crystal $\text{Sr}_2\text{YbSbO}_6$ substrate or a substrate of other composition buffered with a layer of $\text{Sr}_2\text{YbSbO}_6$. Next, the HTSC is patterned by ion milling at a 45° angle. A layer of $\text{Sr}_2\text{YbSbO}_6$ is then deposited. Next, another HTSC layer is deposited and patterned to complete the device.

We wish it to be understood that we do not desire to be limited to the exact details of construction shown and described for obvious modifications will occur to a person skilled in the art.